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SIMULTANEOUS DERIVATIZATION - EXTRACTION TECHNIQUE FOR THE ANALYSIS OF ACIDIC ORGANIC CONTAMINANTS FROM WATER - FEASIBILITY STUDY WITH DIAZOMETHANE FOR THE ANALYSIS OF 4-AMINO - 3,5,6-TRICHLOROPICOLINIC ACID (PICLORAM)

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Picloram (4 amino-3,5,6-trichloropicolinic acid, is a herbicide widely used, for the control of woody and broad leaf plants in pastures, small grains, timberland and various rights of way.

Even though Picloram is highly active at low application rates, is relatively non-toxic to animal species; its wide-spread usage and resistance to degradation raises concerns regarding environmental levels and fate. Various procedures have been developed to determine residues of Picloram in soil, plants, sediments and water. Techniques such as High Performance Liquid Chromatography (HPLC) suitable for the analysis of commercial formulation without derivatization as well as Gas Chromatographic methods which typically determine Picloram as the methyl ester, 2-chloroethyl ester or pentafluorobenzyl derivative. For multicomponent environmental analysis, solvent extraction followed by derivatization and gas chromatographic analysis is the most common technique. However, the performance of these methods, especially in the area of multicomponent environmental applications can be highly erratic and biased low. Recoveries reported by various authors vary from 97(1) to 59(2) percent and it is not uncommon to find values lower than these.

This paper describes the development of a rapid, simultaneous extraction - derivatization procedure (3) for the analysis of picloram in water which provides consistent (>86%) recoveries. The research finding also provides an insight into the possible source of analytical variability related to the chemical properties and equilibrium of Picloram in aqueous solution.

Experimental

Apparatus - Gas Chromatograph Hewlett Packard 5730 with dual Ni63 electron capture detectors. The instrument is fitted with one split/splitless capillary injector system, HP7672A autosampler, HP33804 dual pen strip chart recorder, all interfaced with the HP1000 computer system.

Columns - capillary columns 30m x 0.25mm D1701 and DB1. Temperature program: initial 90 C, hold 2 minutes programming rate 4 C/min, hold at 270 C for 8 minutes. Injector temperature 250 C, Detector temperatures 300 C.

Procedure - unless otherwise stated all experiments were carried out under the following conditions:

- The water spiked or containing the target analytes sample (800 ml) was acidified (HCl) to pH1.
- Dichloromethane (30 ml) was added and mixed well.
- Diethylether (60 ml) was added and mixed well.
- The two layers were allowed to separate and diazomethane (DAM) solution 1 ml (prepared from 21,5g of N,N-Dimethyl N,N-Dinitrosoterephthalamide made up to 37 ml with diethyl ether) was added with a pipette to the top solvent layer in a circular motion.
- The reaction mixture was allowed to stand for 10 minutes.
- The mixture was shaken well and diazomethane addition was repeated twice.
- The mixture was allowed to stand for 2 hours.

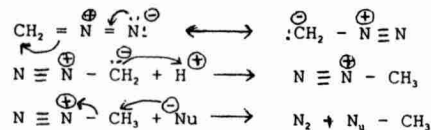
After this, the organic layer was separated and concentrated on a rotary evaporator (addition of more methylene chloride will sink the solvent to form a bottom layer if this is more convenient to separate).

Results and Discussion

Chemical Consideration

Superficial examination of the chemical structure of Picloram, a carboxylic acid with two different amino functions, would make one conclude that it has amphoteric properties. In practice, Picloram behaves as a fairly strong organic carboxylic acid and significant protonation of the amino functions does not occur above pH 0.8. This can be explained by the strong combined electron withdrawing effects of the chlorine and carboxyl substituents (4). The aqueous solubility of Picloram is strongly pH dependent. Even in the narrow range of pH 0.84 to pH 2.68 the solubility increases seven fold from 63 mg/L to 445 mg/L (5). During extraction with an organic solvent it is the undissociated form of Picloram that is extracted. Since both the concentration of undissociated picloram and its aqueous solubility are highly pH dependent, the partition coefficient will also vary with the pH. This may be one of the reasons for erratic recoveries. If Picloram could be derivatized during the extraction step, the formation of a neutral species would shift the complex, simultaneous equilibria in favour of the extraction.

The use of diazomethane was explored during the extraction step to convert Picloram to its methyl ester. It is expected that diazomethane will have a very short lifetime in strong acidic aqueous media because the formation of the protonated reagent is promoted and the latter can react with most nucleophile ($\text{Nu}^{\ominus}$) including water



The presence of extraction solvent in the aqueous reaction mixture will protect diazomethane from rapid decomposition and permit the target reaction to proceed with less competition from non target nucleophiles.

Even if little methyl ester formation takes place in the aqueous phase, portion wise addition of diazomethane to the solvent layer will esterify the already extracted Picloram and extraction of a further quantity of Picloram can begin once again without removing the solvent.

Thus while minimizing the effects of pH on the process, addition of 2-3 portions of diazomethane solution (followed by thorough mixing) becomes practically equivalent with extraction by 2-3 aliquots or organic solvent see Table 1 and 2.

Table 1

RECOVERY OF PICLORAM (SPIKING LEVEL 1ppb) USING DIFFERENT ACIDS AND SIMULTANEOUS DERIVATIZATION/EXTRACTION PROCEDURE.

Acid used at pH (1-2)	% Recovery
H_3PO_4	102
HCLO_4	110
HCOOH	40
H_2SO_4	98,89
HCl	97,106,83*

*Diazomethane added in 1 portion

Recoveries of seven acid herbicides from fortified 800 ml water samples are presented in Table 2.

The recoveries of all seven herbicides were good and ranged from 77 to 111%.

Recovery reproducibility proved excellent.

Table 2

RECOVERIES (%) OF ACID HERBICIDES FROM FORTIFIED (APPROX. $1\mu\text{g/L}$ LEVEL) 800 mL WATER SAMPLES BY SIMULTANEOUS EXTRACTION DERIVATIZATION PROCEDURE

HERBICIDE #1	DAM three portions							AVG	SD	DAM one portion	
	#2	#3	#4	#5	#6	#7				#1	#2
DICAMBA	95	88	90	99		93	97	94	4	87	97
24DP	99	95	98	102	77	97	98	95	8	101	99
24D	111	104	110	113	95	112	111	108	6	116	111
SILVEX	105	100	101	104	86	95	100	99	6	108	95
245T	107	104	105	107	100	101	102	104	3	112	106
24DB	108	104	105	107	104	103	103	105	2	114	107
PICLORAM	101	105	106	100	100	97	97	101	3	86	77

The results in Table 2 show the application of the simultaneous extraction-derivatization procedure to acidic compounds in the full scan including Picloram. The generally excellent recoveries indicated a wide applicability for this technique. Further study is underway for the use of this simple and effective method for other groups of acidic compounds, such as resin and fatty acids. Preliminary results are most encouraging.

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